



Wisconsin
Department of
Natural Resources

Bureau for
Remediation and
Redevelopment

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December 1, 1997
Updated September 5, 2003



Repeal of Temporary Suspension on Approval of and General Interim

Guidance for the Use of Hydrogen Peroxide/Catalyst Injection (a/k/a Fenton's Reagent)

CORRESPONDENCE/MEMORANDUM

State of Wisconsin

DATE: December 1, 1997 FILE REF:

TO: RR Management Team

FROM: Mark F. Giesfeldt - RR/3

SUBJECT: Repeal of Temporary Suspension on Approval of and General Interim Guidance for the Use of Hydrogen Peroxide/Catalyst Injection (a/k/a Fenton's Reagent)

In early August, U.S. EPA sent a letter to all of the Region V states identifying potential concerns regarding the use of hydrogen peroxide/catalyst mixture (Fenton's Reagent) to remediate petroleum contamination at LUST sites. Since they did not provide specific guidance on the conditions under which this technology could be utilized, the R&R Management Team agreed at our August 12-13, 1997 meeting that until further direction was received from EPA, we should temporarily suspend the issuance of approvals using this technology.

On October 27, 1997 we received a letter from U.S. EPA - Region V which provided further direction on the use of Fenton's reagent as a remediation alternative. EPA's letter also includes a copy of a guidance memo prepared by the Florida DEP for their staff regarding the use of this technology (both of these memos are attached for your information). As part of our efforts to further evaluate the use of this technology, we also obtained information from vendors who have patented processes for the injection of Fenton's Reagent and have utilized their technology at numerous remediation projects across the country.

Based on a review of all the available information, we developed guidance on the use of Fenton's Reagent at remediation sites in Wisconsin. As a result, the temporary suspension can now be lifted and the Regions can proceed ahead with approving plans that utilize this technology provided that the attached guidance is followed. We plan to continue gathering information on this process and may provide additional guidance in the future. If you have any questions regarding this memo, please contact Mark Gordon at 608-266-7278.

Attach.

cc: Steve Karklins - DG/2
Rich Roth - DG/2
Joe Renville/Jim Christenson - LS/5
Regional Drinking Water/Groundwater Experts
Andy Tschampa - U.S. EPA Region 5, DRU-7J

DATE: December 1, 1997 FILE REF:

TO: RR Management Team

FROM: Mark Giesfeldt - RR/3

SUBJECT: General Interim Guidance for the Use of Hydrogen Peroxide/Catalyst Injection (a/k/a Fenton's Reagent (FR))

Implementation

All proposals for the injection of FR through injection wells require a prior written approval in accordance with s. NR 812.05, Wis. Adm. Code. Project Managers are expected to follow the MOU between the Drinking Water/Groundwater Program (DG) and RR Programs (attachment 1) when reviewing such proposals. The MOU outlines the general review criteria and the regulatory requirements for all infiltration and injection proposals for remediation.

The final decision on use of the technique should be made on a site-by-site basis, at the discretion of the Project Manager, after consideration of these guidelines, exercising professional judgement. Project Managers may ask for the submittal of additional information prior to granting an approval, deny the request or grant an approval or conditional approval. Adequate information about site conditions should be submitted and reviewed prior to granting an approval. It is expected that most approvals will be conditional.

These guidelines are intended only to assist Project Managers in their review. They are not intended to substitute for a detailed technical review. They should not be attached to or referenced in an approval to substitute for a detailed technical review.

General Guidance

Remediation techniques that use injection of FR will cause an oxidation reaction with organic contaminants of concern in the subsurface, with the goal of removing the contaminants from the environment by oxidizing them into less harmful forms. This technique can be an effective remediation method and may be used at sites, provided the proper precautions are followed, which include, but are not limited to the following. Information on site characteristics needed for use of the technique should be gathered as part of the site investigation under ch. 716, Wis. Adm. Code.

1. The technique should generally not be used in areas where measurable free product or non-aqueous liquids (NAPLs) are present. It may be appropriate to use FR in those areas once the measurable free product or NAPLs are satisfactorily removed. Section NR 140.28(5)(c)4., Wis. Adm. Code, prohibits the injection of materials for remediation where floating non-aqueous phase

liquid is present.¹ One exception to this general prohibition may be sites with deep or contained groundwater where the free product is not floating on the groundwater, such as sinking dense product, where no vapor migration pathways are present or the vapor pressure of the contaminants are low enough not to present a vapor migration risk. For example, it may be appropriate to treat deep, sinking chlorinated hydrocarbon dense NAPLs using FR.

2. Sites with a history of prior contaminant vapor migration to utility trenches, sewers, buildings or other anthropogenic features are not appropriate for use of the technique unless such migration is completely controlled and the appropriate measures are taken to prevent additional migration, as outlined in #3, below.

3. If the reaction could cause any contaminant vapor migration, appropriate measures should be taken to prevent or control that migration. This is especially important for contaminants with high vapor pressures, such as gasoline. If adequate measures will not or can not be taken, the technique should not be used. Such measures include, but are not limited to the following:

- a. All nearby buildings, underground tanks, piping and utilities, sewers, more permeable soil zones and any other anthropogenic or natural features that could act as vapor migration pathways from the treatment zone should be fully identified. Information sources, such as local governments, utilities and "Digger's Hotline" should be contacted to determine the location of underground features. Efforts should be made to locate any unmapped and old anthropogenic features such as abandoned trenches. This could be accomplished using remote sensing techniques, such as ground penetrating radar.
- b. All potential vapor migration pathways should be monitored and/or controlled. Generally, monitoring will involve checking for vapor concentrations using acceptable techniques for the pathway. This may include the use of gas probes and combustible gas meters. Pressure monitoring can provide useful information, as positive soil gas pressure can be an indicator of vapor migration. Temperature monitoring of the subsurface may be advisable when injecting high concentrations of FR under high pressure. Soil vapor extraction systems are the preferred method to control migration in soil and utility trenches; additional measures may be needed to control migration through pipes and sewers, such as forced air venting. It may be necessary to physically excavate/remove/cutoff underground tanks and piping and some types of utility conduits. Generally, controls are preferred over monitoring, but some sites may require both. Recommended factors to consider when evaluating the need for soil venting are outlined in section 1.3.1 (copy attached) of our Guidance for the Design, Installation and Operation of In-Situ Air Sparging Systems.

Where there are nearby buildings that could be in the path of a

¹Section NR 140.28(5) is generally not legally applicable to proposals for the injection of FR, as the injection of this material itself is not normally expected to cause an exceedance of ch. NR 140, Wis. Adm. Code, groundwater quality standards. However, it is still recommended that Project Managers consider requiring proposals to demonstrate that the requirements of s. NR 140.28(5)(c) and (d)1. and 3. through 5., Wis. Adm. Code, are met, because they are considered appropriate from a technical standpoint to FR injection proposals. It may be appropriate to include some or all those requirements, with any appropriate modifications, as conditions of approval.

vapor migration pathway, and there is any question whether such pathways are adequately monitored and/or controlled, it may be necessary to notify building owner/occupants of the planned treatment prior to implementation, provide monitoring within the buildings and, if necessary, evaluate those buildings during the treatment and for an adequate time after treatment.

- c. Exclusion zones should be established around the area to be treated where special safety measures should be taken, including the control of possible ignition sources, such as switches, motors and electrical equipment and the use of intrinsically safe equipment and tools.

Attached are U.S. EPA's general recommendations on this technology outlined in a letter to Mark Giesfeldt dated October 27, 1997 (attachment 2) and an attachment to that letter, which is the State of Florida's safety guidelines (attachment 3). We believe the U.S. EPA and Florida guidelines are generally consistent, from a technical standpoint, with our guidelines. We suggest that their guidelines be consulted by Project Managers when performing technical reviews of FR injection proposals. We also prepared the following comments to help clarify their guidelines.

U.S. EPA Letter

1. We formally requested their guidance in an October 14, 1997 letter from Mark Giesfeldt to Norm Niedergang. We have also contacted U.S. EPA's Technology Innovation Office and the Interstate Technology Resource Center (ITRC) for available information on the technology and have not yet received any information from those sources.

2. The U.S. EPA document on evaluating alternate cleanup technologies for UGST sites has been distributed to the Regions. In our opinion, the chapter on air sparging is of limited use, given the differences between the technologies. However, some of the safety and monitoring measures outlined may be useful. Our guidance on air sparging as prepared by George Mickelson may be of more value, and we refer to it in our guidelines. The flow chart referred to from the U.S. EPA guidance (Exhibit VII-3) was not provided with U.S. EPA's letter for some reason. A copy of that chart is attached.

3. U.S. EPA mentions fracturing as a concern with the injection process. We agree this can occur and is of concern. This can occur in certain types of formations and only under certain higher injection pressures, but not necessarily in all formations under all pressures. We understand that various vendors who use FR have different techniques for injecting it into the subsurface, and pressures can vary from vendor to vendor.

Florida DEP Memo

1. Florida recommendations g. and h. discuss temperature monitoring. This may be more important in Florida where ambient soil and groundwater temperatures are higher than in Wisconsin. Temperature monitoring may be more important when the vendor uses high concentration FR and/or higher pressure injection techniques.

Please contact Gary Edelstein or Terry Evanson if you have any questions about this guidance.

Attach.

MFG:GAE:TAE

Note to user: These attachments to the cover memo for publication RR583 are from scans of hard copy documents. Efforts have been made to make them as accurate as possible. However, they are not exact copies and may have some minor differences as compared to the originals. If you would like to have attachments that are completely accurate copies, please request an original hard copy.

Attachment 1

CORRESPONDENCE/MEMORANDUM

State of Wisconsin

DATE: May 7, 1996

TO: Emergency and Remedial Response Program Staff

FROM: Paul Didier - SW/3 Bob Krill - WS/2
Mary Jo Kopecky - WW/2 Bruce Baker - WR/2

SUBJECT: Policy on the Approval of Infiltration Systems and Injection Wells for Soil, Groundwater or Aquifer Remediation.

MEMORANDUM OF UNDERSTANDING

This Memorandum of Understanding (MOU) establishes the basic responsibilities of Department of Natural Resources (DNR) staff in the Solid and Hazardous Waste Management (SW), Wastewater Management (WW), Water Resources Management (WEM), and Water Supply (WS) programs with respect to Department review and approval of requests to use infiltration systems or injection wells for the remediation of contaminated soils, aquifers or groundwater. Specifically covered within the scope of this MOU is staff approval of any request to allow the insitu infiltration or injection of a "remedial material" as it is defined in section NR 140.05 (20k) of the Wisconsin Administrative Code.

Historically, the use of a well or drillhole for the underground placement of any "substance" has been prohibited under provisions of Wisconsin's private well code since the 1930's. However, on October 1, 1994, s. NR 812.05, Wis. Adm. Code, was modified to allow the DNR to approve such placement when it is determined to be necessary for the remediation of soil, groundwater or aquifer contamination. "Substance," as it is defined in this section of the state administrative code, means "... any solid, liquid, semisolid, dissolved solid or gaseous material, naturally occurring or manmade chemical, parameter for measurement of water quality or biological organism which, in its original form, or as a metabolite or a degradation or waste product, may decrease the quality of groundwater" (s. 160.01 (8), Stats.).

Under the provisions set forth in this MOU, staff assigned to the Emergency and Remedial Response (ERR) Section in the SW program will retain lead responsibilities for DNR oversight of soil, groundwater or aquifer remediation activities and may approve the use of a remedial infiltration system or remedial injection well system after taking into consideration the following:

I. General Proposal Review

Prior to approval, any proposal which calls for the use of a remedial infiltration system or injection well shall be reviewed to ensure that:

- a. infiltration systems and injection wells are designed to operate effectively.
- b. the infiltration or injection of a substance or a remedial material is required as part of a remedial treatment scheme and that the substance or remedial material introduced will not increase the severity of the existing contamination or permanently impair future use of the affected soil, aquifer

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or groundwater;

- c. the type, concentration, and/or volume of the infiltrated or injected substance or remedial material is limited to the extent necessary for restoration of the contaminated soil, aquifer or groundwater;
- d. any by-product formed as a result of remediation processes will either be recaptured or further degraded to a point where it does not constitute further risk to either human health or the environment;
- e. environmental contaminants and all infiltrated or injected substances and remedial materials shall be controlled such that clean-up of the contaminated media is achieved and the boundaries of the impacted area are not significantly expanded during, or as a result of, the proposed remedial action;
- f. maximum limits on soil concentration and/or water quality are established for any infiltrated or injected substances or remedial materials which are not covered under a Wisconsin Pollutant Discharge Elimination System (WPDES) permit; and
- g. monitoring of the remedial activities will be sufficient to verify the performance of the infiltration or injection devices and the effectiveness of all required contaminant containment measures.

II. Wastewater Requirements

According to s. 147.02 (1) Stats., the discharge of any pollutant from a point source to the waters of the state is prohibited unless it is done under a WPDES permit issued by the DNR. Well injection or infiltration of a substance or remedial material that would be considered a contaminant if otherwise detected in a groundwater or surface water resource constitutes a "discharge" and requires that a WPDES permit be issued.

The Wastewater Program has developed a generalized permit which streamlines the review and permitting process for wastewater discharges from soil or groundwater remediation projects. In most cases, contaminated groundwater discharges from remedial action operations will be eligible for coverage under the WPDES general permit; however, an individual WPDES permit containing site-specific discharge and monitoring requirements may be issued at the request of the permittee, the ERR program or as otherwise determined by the WW program.

District ERR project managers shall consult with the district WW program supervisor to obtain a WPDES permit during the remedial project approval process.

NOTE: (A) Injection of a substance or a remedial material through a well or drillhole solely for the purpose of waste disposal **is prohibited**. In those cases where well injection solely for the purposes of waste disposal would be necessary to achieve the objectives of a remediation effort, a written variance issued by the district WS

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program supervisor shall be obtained in addition to the WPDES permit.

(B) Waste disposal via an infiltration system, such as a subsurface soil absorption system, is allowed under a WPDES permit and does not require a WS variance.

III. Hazardous Waste Requirements

Section NR 600.04 (1), Wis. Adm. Code, prohibits the underground injection of a hazardous waste through a well. The discharge of hazardous wastes to land treatment systems, including subsurface soil absorption fields, is prohibited under s. HR 214.04 (2), Wis. Adm. Code.

A "hazardous waste" is defined as any solid waste which is not excluded from regulation as a hazardous waste under s. NR 605.05 (1), Wis. Adm. Code, and which meets any of the following criteria:

- a. It is listed in s. HR 605.09 as a hazardous waste and has not been excluded from the list under s. NR 605.10.
- b. It exhibits any of the characteristics of hazardous waste identified in s. HR 605.08.
- c. It is a mixture of solid waste and one or more hazardous wastes listed in s. NR 605.09 and has not been excluded under s. HR 605.10.

There is an exclusion in the "solid waste" definition in section 144.01 (15), Stats., for "solid or dissolved materials in industrial discharges which are point sources subject to permits under ch. 147." The definition of a hazardous waste in s. NR 605.04, Wis. Adm. Code, requires that a material must first be a "solid waste." Thus, groundwater discharges which are subject to regulation under a WPDES permit are not considered to be a solid or hazardous waste and are not subject to the injection well or land treatment prohibitions.

NOTE: The industrial discharges exclusion only applies to the actual point source discharge. It does not exclude industrial wastewaters while they are being collected, stored or treated before discharge, nor does it exclude treatment residuals generated by industrial wastewater.

Groundwater that is removed from the environment and which has a hazardous waste characteristic (s. NR 605.08, Wis. Adm. Code) or which meets or exceeds PALs due to contamination from releases of listed hazardous waste (s. NR 605.09, Wis. Adm. Code) is subject to regulation as a hazardous waste prior to being discharged back into the ground under a WPDES permit. There are, however, regulatory exemptions to some of the Hazardous Waste (HW) program's regulations which apply to contaminated groundwater from certain federally regulated leaking underground petroleum storage tanks (s. NR 605.05 (1)(q), Wis. Adm. Code] and to the storage and treatment of groundwater in "wastewater treatment units" (ss. NR 600.03 (261) and NR 630.04 (1), Wis. Adm. Code].

District ERR project managers shall consult with the district HW program supervisor prior to approval of any infiltration or injection proposal to

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ensure that compliance with all applicable state and federal hazardous waste regulations is maintained.

IV. Groundwater Protection Requirements

Section 144.951, Stats., requires that the DNR shall be in compliance with Wisconsin's Groundwater Law (ch. 160, Stats.) in the administration of any program, responsibility or activity which is assigned or delegated to the department. Therefore, all proposed remedial infiltration and injection practices must adhere to the requirements of ch. 160, Stats., and the administrative rules established in ch. HR 140, Wis. Adm. Code.

The following points should be considered during the review of any remedial infiltration or injection proposal:

- a. Activities must be performed such that human health, welfare, and the environment are protected.
- b. Where technically and economically feasible, the concentrations of substances or remedial materials which are infiltrated or injected during restorative processes and any degradation by-products that are created as a result of remedial activities will be reduced to preventive action levels (PALS) specified in ch. NR 140 within a reasonable period of time.
- c. If the PAL or ES for any infiltrated or injected substance or remedial material listed in ch. HR 140 will be attained or exceeded in groundwater at any point of standards application, a temporary exemption under s. HR 140.28 (5), Wis. Adm. Code, is required.
- d. If a substance or remedial material that is not currently listed in ch. HR 140 is to be infiltrated or injected, a temporary exemption under s. HR 140.28 (5), Wis. Adm. Code, is required.

Approval of all Chapter HR 140 temporary exemption requests shall be coordinated with the Groundwater Management Section of the WRM program (Contact: Steve Karklins, WR/2).

NOTE: A temporary exemption is not required when a substance or remedial material is to be .

1. injected or infiltrated at a concentration below its designated groundwater PAL; or
2. infiltrated, not injected, at an alternative infiltration discharge limit approved in a discharge management plan under a WPDES permit so that PALS will not be exceeded at any point of groundwater standards application; or
3. used exclusively for oxygen delivery (i.e. air, O₂ gas, hydrogen peroxide, or slow release oxygen compounds); or

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4. infiltrated as part of a soil remedy and will not reach the saturated zone.

The requirements or conditions of the temporary exemption, as well as the responsibilities of the program staff, will be defined in guidance documents developed jointly by all of the affected programs. District ERR project managers should not approve the infiltration or injection of any substance or remedial material which is not addressed through a WPDES permit, allowed under a ch. NR 140 temporary exemption, or otherwise recommended in an ERR guidance document until after consulting with ERR staff in the central office.

V. Water Supply Protection Requirements

Part C of the Safe Drinking Water Act (PL 93-523) requires that each state administer an Underground Injection Control (UIC) program which protects all. underground sources of drinking water from contamination which may result from the subsurface placement of fluids via injection wells. The two primary requirements imposed by federal UIC regulations are: (1) maintenance of a statewide inventory of underground injection practices and (2) approval or permitting of only those infiltration or injection practices which do not endanger drinking water supplies.

NOTE: "Endangerment" is defined as "the movement of fluid containing any contaminant into an underground source of drinking water, if the presence of that contaminant may cause a violation of any primary drinking water regulation or may adversely affect the health of persons." [40 CFR 144.1 (g)]

Therefore, in addition to the requirements identified in the preceeding sections, the WS program shall be consulted if any of the following situations are to occur:

- a. Substances or remedial material are to be injected into any well which was originally constructed to provide a potable water supply. Concurrence for such injection shall be obtained from the district WS program supervisor prior to approval of the remedial action plan.
- b. A remedial infiltration system or injection well will be located within 100 feet of any public or private water supply well. The well owner and the district WS program supervisor shall be notified of the proposed remedial activities, the anticipated impact of these activities on local groundwater quality, and the measures which will be employed to evaluate the effectiveness of the clean-up effort.
- c. A remedial infiltration system or injection well will be located within the wellhead protection area established for any public water supply well. The well owner, manager of the wellhead protection area, and the district WS program supervisor shall be notified of the proposed remedial activities, the anticipated impact of these activities on local groundwater quality, and the measures which will be

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employed to evaluate the effectiveness of the clean-up effort.

Upon completion of remedial activities which require the use of injection wells, all injection wells shall be closed and properly abandoned in accordance with the applicable requirements for well, drillhole or borehole abandonment established by the Department.³

NOTE: For each injection well that is abandoned, a well abandonment form (Form 3300-SB or 3300-SW) shall be completed and submitted to the Department.⁴

SUMMARY

District ERR project managers may approve a request to use a remedial infiltration system or injection well in accordance with the requirements and conditions listed above. ERR staff assigned to the DNR's central office will be responsible for the review and approval of any infiltration or injection request which will not be directly overseen by district ERR staff.

All ERR project approvals which authorize the use of a remedial infiltration system or injection well shall be in writing and copied to the district WS program supervisor and to the Bureau of Water Supply's UIC program Coordinator.

The Bureau of Water Supply will provide the necessary reporting of these activities to the United States Environmental Protection Agency's UIC staff in Region 5.

Approved:

Paul P. Didier, Director, Bureau
of Solid & Hazardous Waste
Management

Mary Jo Kopecky, Director
Bureau of Wastewater Management

Robert M. Krill, Director
Bureau of Water Supply

Bruce Baker, Director
Bureau of Water Resources
Management

Footnotes

1 An advisory guidance document listing recommended design criteria and suggested operational guidelines for remedial injection wells and infiltration systems is being developed by staff in the SW program's Emergency and Remedial Response Section. Until this document is published, district ERR project managers should refer to George Mickelson's (SW/3) August 1, 1995, memo entitled "Recommendations for Injection Well Design and Operation for Insitu Bioremediation Projects" to help ensure statewide consistency in the proposal review process. District ERR project managers should also consult with ERR

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program staff in the central office for assistance in identifying and addressing any additional issues which may need to be considered.

NOTE: If specific design or operational conditions are to be required as part of the approval process, those requirements will need to be established through the adoption or amendment of administrative rules.

2 Refer to the Guidance entitled "Identifying the Wellhead Protection Area of a Public Water Supply Well" for further instructions on how to delineate a wellhead protection area.

3 The well and borehole abandonment requirements which are found in ch. NR 141. Wis. Adm. Code, apply to monitoring wells and boreholes that are regulated by the Department under chapters 144, 147 or 160, Stats., or in permits, plan approvals or orders issued under the authority of those chapters. All other wells and boreholes shall be abandoned according to the provisions of ch. NR 812, Wis. Adm. Code.

4 Completed well abandonment forms should be submitted to the district WS program. A photocopy of the completed abandonment form should also be sent to the Underground Injection Control program in the DNR's Bureau of Water Supply, P.O. Box 7921, Madison, WI 53707-7921.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5
77 WEST JACKSON BOULEVARD
CHICAGO, IL 60604-3590

Oct 27 1997

REPLY TO THE ATTENTION OF: D—8J

Mr. Mark Giesfeldt
Director
Bureau of Remediation and Development
Wisconsin Department of
Natural Resources
Post Office Box 7921
Madison, Wisconsin 53707-7921

Re: Hydrogen Peroxide/Catalyst Injection

Dear Mr. Giesfeldt:

This letter is in response to your letter of October 14, 1997, in which you requested further direction on the use of hydrogen peroxide/catalyst mixture injection for remediation of petroleum leaking underground storage tank (LUST) sites. We commend the State for seeking to gather additional information concerning this technology. Since late this summer, we have attempted to gather additional information as well. However, it was not clear to us, based on our conversations, that the State had formally requested such guidance. The following suggested guidelines are provided with LUST sites in mind. Other considerations may come into play at sites involving contamination other than petroleum. In addition, we have not reached any conclusions about the applicability of this technology to particular types of sites. These suggestions are in no means meant to limit the State's ability to develop guidelines for the use of this technology within the State of Wisconsin and subject to the State's oversight.

I should begin by indicating that the United States Environmental Protection Agency encourages the use of innovative site characterization and corrective action techniques to remediate all types of environmental contamination sites. However, it is

also important to emphasize that proper controls should be placed on any and all techniques, which could have adverse effects on the surrounding environment.

For the preparation of these suggestions, we have reviewed materials presented to us by a contractor that uses the referenced method and U.S. EPA materials concerning similar technologies, and we have contacted personnel in our Headquarters' Office. The information we have uncovered to date indicates that the process can be effective at remediating certain types of contaminants. As the technology involves an exothermic reaction and is fairly new to our program, we are particularly concerned that effective controls are in place to mitigate potential impacts resulting from that reaction.

As guidance, I would refer you to Chapter VII of the U.S. EPA guidance document entitled "How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites A Guide for Corrective Action Plan Reviewers" (EPA 510-B-95-007, May 1995) Chapter VII describes and provides recommendations on the use of Air Sparging, a process which injects air into the subsurface, which is sometimes used to remediate petroleum LUST sites. We recommend referring to the recommendations related to Air Sparging, as we think control measures recommended for Air Sparging may be germane to the injection of a hydrogen peroxide/catalyst mixture.

We understand, however, that there is a fundamental difference between these two technologies. While they both involve injection, the peroxide/catalyst solution involves a chemical reaction in both soil and groundwater, whereas air sparging involves volatilization of petroleum constituents in groundwater. An adequate site characterization will determine if there are other chemicals in the subsurface which may react with the hydrogen peroxide/catalyst mixture.

Exhibit VII-3 (attached) is a flow chart describing the initial screening which should be conducted prior to implementation to determine the effectiveness of Air Sparging. In our opinion, the forced injection of air or any other material into the ground should lead to similar physical concerns and criteria. As you are aware, there are other injection concerns (exceedence of primary or secondary safe drinking water contaminants), which are usually addressed under separate Underground Injection Control permits.

Based on the review we have conducted so far, we would suggest that utilization of this technology in some of the situations listed below might not be appropriate and that these considerations should be kept in mind in reviewing applications for the use of this technology. Specific suggested limitations are as follows:

1. We suggest the injection of the Hydrogen Peroxide/Catalyst mixture may not be appropriate where there is measurable free product present in the anticipated radius of influence of the injection area. An exception might be when it is used at an isolated or rural site with no utilities or manmade conduits present.

2. The Hydrogen Peroxide/Catalyst mixture may be used at LUST sites where the primary contaminant is gasoline, assuming site conditions are appropriate for its use. It may not be appropriate for use in urban areas with utilities and manmade conduits in the anticipated radius of influence of the injection area. The literature search we have conducted indicates that the process seems to be effective at remediating dissolved gasoline constituents in groundwater, but the higher vapor pressures of these constituents could cause unwanted migration of vapors outside the reaction zone. Examples of contaminants it might be preferable to use this technique on include heating oil, diesel fuel, waste oil and less volatile chlorinated solvent releases. This technology might be appropriate at sites involving these contaminants where its effectiveness has been demonstrated and where vapor migration concerns are not as strong as they are at the more volatile contaminated sites. This determination should be made on a site-specific basis.

3. If the Hydrogen Peroxide/Catalyst mixture is going to be used at a site, a thorough utility search should be conducted. If it is determined that a utility conduit or other potential pathway might be impacted by an injection point, the utility should either be monitored for vapor migration of the constituent being remediated (or residual by products of the reaction), or the injection point should be surrounded with sufficient vapor extraction capture points to prevent unwanted migration. An adequate site characterization should be completed to help guide the location of the injection, extraction or monitoring points.

4. We suggest the injection of the Hydrogen Peroxide/Catalyst mixture may not be appropriate at sites where there have been

documented cases of petroleum vapors present in buildings or utilities in the immediate area.

5. The Hydrogen Peroxide/Catalyst mixture may be used in a confined aquifer system when the system is below reasonably anticipated manmade utility trenches or conduits (an example is the demonstration site at the Savannah River site where the process was used at a depth of approximately 135 feet below grade)

6. As with any remediation technique, the specific geology/hydrogeology must be fully understood and adequately characterized before using the Hydrogen Peroxide/Catalyst mixture at a site. Adequate characterization is a site specific determination made in consultation with the regulatory case manager. This is especially true, considering the tendency for the injection process to create hydraulic fracturing of the sub-surface, thereby increasing permeability around injection points.

This list is not intended to be all inclusive and may be modified as more information is obtained and reviewed. We are willing to work with you and other State agencies as you and they develop guidance on this or any other LUST remediation technique. In fact, enclosed is a copy of a guidance memo from the Florida Department of Environmental Protection which deals with this issue and you may find helpful.

We believe that the Hydrogen Peroxide/Catalyst mixture injection process can be an effective remediation process, if used under appropriate conditions. Finally, when injecting any material into the ground, vapors or free product may migrate outside of the reaction or treatment zone. The use of Soil Vapor Extraction to control migration should always be considered in conjunction with this technology.

If you require further assistance, please call Andrew Tschampa, Chief of the Underground Storage Tank Section at (312) 886-6159 or Gilberto Alvarez, of the USTS at (312) 886-6143.

Sincerely yours,
Norman R. Niedergang, Director
Waste, Pesticides and Toxics Division

Attachment 3

Florida Department of

MemorandumEnvironmental Protection

TO: DEP District Offices and Local Programs

FROM: Michael Sole, Chief
Bureau of Petroleum Storage Systems

DATE: October 9, 1997

SUBJECT: In Situ Chemical Oxidation Safety Advisory

A sewer and home explosion resulting in one fatality and injuries to three other persons occurred recently in Wisconsin (EPA Region 5). A petroleum contaminated site, approximately one block away, was under remediation at the time, involving an in situ chemical oxidation method which uses hydrogen peroxide and a proprietary catalyst.

The incident is under investigation. One of the possible sources that may have contributed to the explosion is the migration of vapors through a municipal sewer line, which has had a 20 year history of gasoline contamination, and which runs past the remediation site to the home. The investigation is still underway, so no conclusions have been drawn.

EPA has advised all region 5 leaking underground storage tank programs to proceed carefully prior to approving the use of this technology, and an effort is underway to outline site-specific criteria that should be considered prior to its use.

At this time, in situ chemical oxidation methods for the remediation of petroleum contaminated sites in Florida is not widespread, but efforts are underway by several remediation firms to make greater use of it. The Department of Environmental Protection does not believe that the use of the method should be discouraged in Florida, but like EPA, advises that all Department, district, and local programs proceed carefully in reviewing and approving plans prescribing it. The Department's advisory applies to any in situ chemical oxidation method, involving any type of catalysts and oxidants that react exothermically and raise the subsurface temperature.

Since the volatility of petroleum hydrocarbons is sensitive to temperature, there could be a significant change in both the concentration and distribution of flammable vapors when using an in situ chemical oxidation method. This dynamic environment is less predictable than most other cleanup situations, where less powerful remediation methods are unable to drive the cleanup by

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greatly changing a site's established equilibrium of hydrocarbons amongst the vapor, liquid, and adsorbed phases. The drawback, however, is that a greater amount of oversight may be needed to maintain control.

As is the case in any petroleum or flammable solvent remediation effort, design considerations must take potential fire and explosion hazards into consideration, so that appropriate equipment and operating procedures can be specified for their prevention. The current issue of the Remedial Action Plan Checklist recognizes that any petroleum remediation site can have the potential for a fire or explosion, so it includes reminders regarding the following items: migration via underground conduits and utilities; lower explosive level (LEL); National Electrical Code practices intended to minimize ignitions from electrical devices; explosion-proof motors; spark-resistant material of construction for vapor blower housings and impellers; and in the case of thermal oxidizers, items to consider for the prevention of furnace explosions.

The Bureau of Petroleum Storage Systems will not wait for the results and conclusion of the Wisconsin incident investigation to set forth guidance. The Remedial Action Plan Checklist for petroleum cleanup sites will be revised to include a section addressing in situ chemical oxidation. Until the checklist can be revised, the items listed below should be helpful to preparers and reviewers of in situ chemical oxidation remediation plans in identifying potential fire and explosion hazards. The suggested items to consider are, but not necessarily limited to:

- a. the potential for subsurface migration of vapors, either through pathways in the aquifer and soil itself, or via underground conduits such as sewer lines, utilities, storm drains, etc., and the destination of those pathways should migration occur;
- b. the presence of free product in the subsurface, either in underground utilities, or in the form of non-aqueous phase liquids, which could be volatilized by the heat of an exothermic chemical reaction, in concentrations which exceed the lower explosive level;
- c. the presence of underground petroleum storage tanks and petroleum dispenser pipelines which may be near the source of heat generated by chemical oxidation reactions, and measures to prevent them from exposure to excessive amounts of heat;

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- d. identification and control of possible ignition sources (electrical equipment, devices, and switches, vehicle exhaust sparks, mechanical sources of sparks, etc.) at potential vapor migration pathway destinations;
- e. monitoring of vapor concentrations, for comparison with lower explosive levels, at the site and/or in conduits and other potential pathways during operation of the chemical oxidation system;
- f. the chemical reactants involved and the amount of heat liberated by their reaction;
- g. monitoring of aquifer and/or vadose temperature during treatment;
- h. a maximum temperature that may be tolerated before shutting down the operation is necessary;
- i. control of reactant concentrations and/or quantities as a means of controlling temperature;
- j. the possibility of using a vacuum extraction system to collect vapors at sites where significant amounts of volatilization is expected to occur; and
- k. safety of workers involved with the actual handling of chemicals.

The foregoing list should not be applied in blanket fashion, and technical judgments should be made on a site-specific basis. Technical questions may be directed to Rick Ruscito, P.E., at the Department's Tallahassee headquarters, telephone 850/487-3299.

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